Thermochimica Acta, 224 (1993) 151–163
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) hydroxy-*p*-toluenesulphonates

Mercedes Bombín [a,1], MªA. Martinez-Zaporta [a], Araceli Ramírez [a], Alejandro Guerrero [a] and Antonio Jerez Mendez [b,*]

[a] *Instituto de Ciencia de Materiales, Sede D. C.S.I.C., Serrano 113, 28006 Madrid (Spain)*
[b] *Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid (Spain)*

(Received 22 January 1993; accepted 17 February 1993)

Abstract

The thermal behaviours of Co(II), Ni(II), Cu(II), Zn(II) Cd(II) and Pb(II) hydroxy-*p*-toluenesulphonates were studied by simultaneous thermoanalytical methods (DTA, TG). The measurements were at times supplemented by X-ray analysis of the decomposition products. The decomposition processes of the samples were carried out in air and in nitrogen atmospheres.

INTRODUCTION

Several heavy, transition metallic salts of sulphonic acids have yet to be characterized, especially their thermal behaviour. Charbonnier [1] has studied the thermal decomposition of cobalt alkanesulphonates. Meisel et al. [2] reported on the thermal analysis of the thermal decomposition of some transition metal benzenesulphonates.

In the last five years, we have studied the synthesis, properties and crystal structures of different metallic sulphonates [3–6]. As part of this general program, we have reported the thermal degradation of β-napthalenesulphonic and 1,5-naphthalenedisulphonic acids, and their corresponding copper salts [7], the thermal behaviour of cobalt, copper and zinc methanesulphonates [8], the thermal decomposition of Co, Ni, Cu, Zn, Cd and Pb *p*-toluenesulphonates [9], and, recently, we have reported the synthesis, characterization and thermal decomposition of benzene-disulphonates (BDS) of these transition metals [10].

Here we report the thermal decomposition of the hydroxy-*p*-toluene-

---

* Corresponding author.

[1] Present address: Departmento de Química Analítica e Ingeniería Química, Facultad de Ciencias, Universidad de Alcalá de Henares Ctra, Madrid-Barcelona Km 33.6, Alcalá de Henares, Madrid, Spain.

sulphonates of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II). These hydroxysalts, of general formula $M_p(A)_q(OH)_r$, are products of the hydrolysis of the *p*-toluenesulphonates, and have not yet been described in the literature.

EXPERIMENTAL

Synthesis

The basic salts have very low solubilities; therefore, the composition and properties of the solid formed are greatly dependent on the synthesis conditions such as the concentration of the solution, the precipitation rate, the temperature, the aging time, etc.

The relationships between the precipitate and the supernatant solution [11–13] have been applied in the present case. The determined expressions are referred to the operational method known as 'fixed volume' [13] and allows us to know the composition of the precipitate and the supernatant solution.

The synthesis of the hydroxy-*p*-toluenesulphonates was carried out in aqueous solution following several hydrolytical procedures. In one procedure, the starting solution was the corresponding neutral salt solution which was treated with alkaline agents until partial hydrolysis of the salts was attained. The general reaction can be written.

$$\frac{p}{Z_A} A_{ZM} M_{ZA} + r OH^- \rightarrow M_p(A)_q(OH)_r + \frac{r}{Z_A} A^-_{ZA} \qquad (1)$$

In another procedure, the reaction took place between a suspension of the hydroxide or oxides with *p*-toluenesulphonic acid, without complete neutralization. This reaction is

$$p M(OH)_{ZM} + q AH_{ZA} \rightarrow M_p(A)_q(OH)_r + Z_A q H_2O \qquad (2)$$

where M is Co, Ni, Cu, Zn, Cd, or Pb. The relation $pZ_M = qZ_A + r$ also takes place in both cases. Z_M is cation valence and Z_A is anion valence.

Throughout this paper, CH_3–C_6H_4–SO_3^- is written as *p*-TS^-.

The metal contents were determined by EDTA complexometry, employing NET (for Zn, Cd and Pb) and murexide (for Co, Ni and Cu) as indicators. The anion determination was performed with a Perkin-Elmer 240B microanalyser.

The compounds obtained were characterized by chemical analysis: the cations were determined by EDTA complexometry, employing NET (for Zn, Cd and Pb) and murexide (for Co, Ni and Cu) as indicators; the anion determination was performed with acid cationic exchange resins, and titration of the eluted acid with NaOH.

After being analysed and characterized by X-ray diffraction and IR spectra, the compound were identified as $Co_5(p\text{-}TS)_2(OH)_8 \cdot 2H_2O$; $Ni_5(p\text{-}TS)_2(OH)_8 \cdot 2H_2O$; $Cu_2(p\text{-}TS)(OH)_3$; $Zn_5(p\text{-}TS)_2(OH)_8 \cdot 4H_2O$; $Cd_2(p\text{-}TS)(OH)_3 \cdot 2H_2O$; $Pb(p\text{-}TS)(OH)$; and $Pb_2(p\text{-}TS)(OH)_3$.

Instrumentation

TG and DTA experiments were recorded on a Stanton 781 system, with a heating rate of 10°C min^{-1} in still air and flowing N_2 (50 ml min^{-1}). Platinum–rhodium crucibles were used, with Al_2O_3 as reference material. The samples, about 10 mg, were pyrolysed up to 1000°C.

Some experiment were performed in a Du Pont 951 thermobalace attached to a Du Pont 990 unit.

The individual residues of the decomposition were identified by means of X-ray diffraction by the powder method in a Siemmens K-810 diffractometer with a D-500 goniometer using Cu Kα radiation.

In some cases, IR spectra were used for identification, recorded on a Perkin-Elmer 580B spectrophotometer in the range 4000–200 cm^{-1}.

RESULTS AND DISCUSSION

All the samples studied show similar behaviour.

The decompositions in air atmosphere take place in three processes. The first stage is the dehydration of the compounds (except for those that are anhydrous) between 100 and 200°C. The anhydrous salts are stable up to about 250–550°C. At those temperatures, the DTA curves show a complex exothermic effect corresponding to the dehydroxylation and the combustion of the organic radical, resulting, in general, in the metallic sulphates. When these sulphates are formed, there is generally another endothermic process at about 750–800°C, resulting in the corresponding oxides.

When the treatments are carried out in N_2 flow, the dehydration process occurs in the same way as in air. Between 300 and 600°C, there are generally two overlapping endothermic effects due to the dehydroxylation and the decomposition of the organic group, leading to a mixture of metallic sulphides, the metal and carbon, or the metal and carbon.

$Co_5(p\text{-}TS)_2(OH)_8 \cdot 2H_2O$

In static air (Fig. 1(a))

The elimination of the water molecules occurs between 100 and 200°C, and the DTA curve shows an endothermic effect indicating formation of the anhydrous hydroxysalt, according to the reaction

$$Co_5(p\text{-}TS)_2(OH)_8 \cdot 2H_2O \rightarrow Co_5(p\text{-}TS)_2(OH)_8 + 2H_2O$$

(Weight loss: experimental, 8.33%, calculated, 8.43%.)

Decomposition of the anhydrous hydroxysalt starts at 200°C and is complete at 500°C. The DTA curve shows several simultaneous processes, with a large overall exothermic effect corresponding to the dehydroxylation and the anion combustion. The residue at 500°C, indentified by X-ray

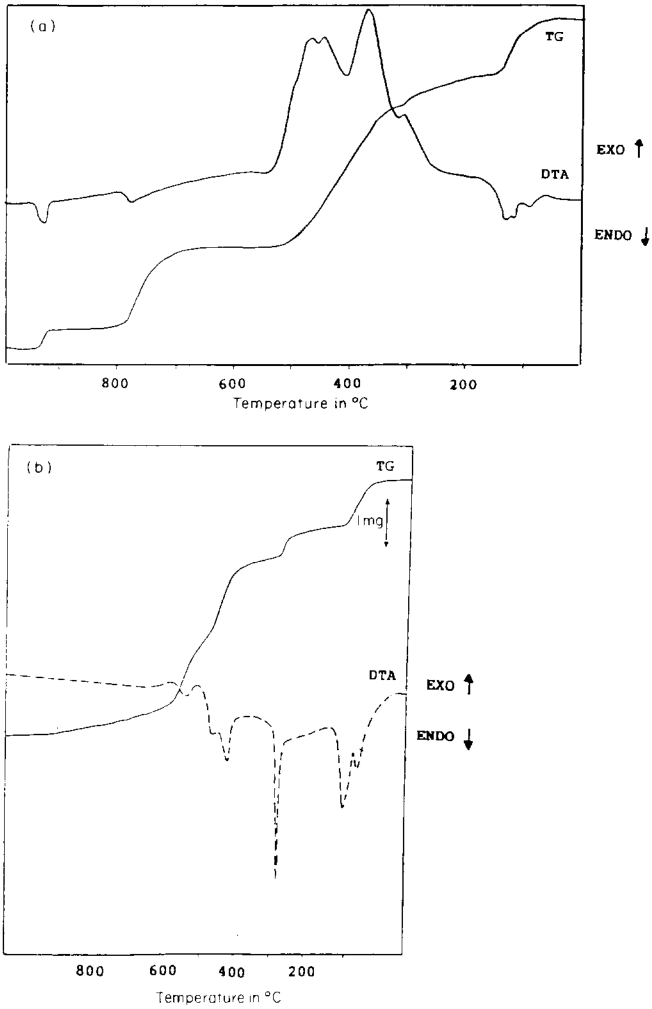

Fig. 1. TG and DTA curves for $Co_5(p\text{-}TS)_2(OH)_8 \cdot 2H_2O$: (a) in static air; (b) in flowing N_2.

diffractometry, was a mixture of β-$CoSO_4$ (ASTM 28-386) and Co_3O_4 (ASTM 9-418).

Between 650 and 750°C, β-$CoSO_4$ decomposes and the residue is Co_3O_4 (ASTM 9-418).

Finally, in the last process, there is an endothermic peak at 900°C corresponding to the transformation of the Co_3O_4 to CoO (ASTM 9-402) (Total weight loss: experimental, 55.6%; calculated, 54.2%.)

In flowing nitrogen (Fig. 1(b))

The first step, dehydration, occurs in the same way as in air. (Weight loss: experimental, 8.90%; calculated, 8.43%.)

Decomposition of the anydrous cobalt hydroxy-*p*-toluenesulphonate takes place between 200 and 300°C, according to the reaction:

$Co_5(p\text{-TS})_2(OH)_8 \rightarrow Co_5(p\text{-TS})_2O_4 + 4H_2O$

(Weight loss: calculated, 7.95%, experimental, 7.62%.)

The residue at 320°C, the oxy salt, was amorphous to X-ray diffractometry; its IR spectrum does not show the characteristic band of non-associated OH^-.

Anion decomposition, registered in DTA curve as two endothermic processes, starts at about 400°C, and finishes at 600°C. The residue was amorphous to X-ray diffractometry.

Finally, there is a continuous weight loss, with the final residue at 1000°C being Co metal (ASTM 15-806) and traces of carbon black.

$Ni_5(p\text{-TS})_2(OH)_8 \cdot 2H_2O$

In static air (Fig. 2(a))

The hydroxy salt is stable up to 90°C; between this temperature and 150°C, the DTA curve shows an endothermic effect corresponding to the loss of the two water molecules:

$Ni_5(p\text{-TS})_2(OH)_8 \cdot 2H_2O \rightarrow Ni_5(p\text{-TS})_2(OH)_8 + 2H_2O$

(Weight loss: calculated, 4.51%; experimental, 4·45%.)

The anhydrous hydroxy salt starts to decompose at ≈350°C, where the DTA curve shows an exothermic effect corresponding to the dehydroxylation and the combustion of the organic group in a simultaneous process, finishing at 500°C. The residue at this temperature, identified by X-ray diffractometry, is a mixture of NiO (ASTM 4-0835) and $NiSO_4$ (ASTM 13-435).

At about 700°C, $NiSO_4$ decomposes and the final residue at 900°C is NiO.

In flowing nitrogen (Fig. 2(b))

When the experiment was carried out in an inert atmosphere, the decomposition temperatures were similar to those found in air atmosphere. The DTA curve shows two endothermic processes, dehydration and a simultaneous effect between 350 and 600°C, due to the dehydroxylation and the anion decomposition.

The final residue at 1000°C was identified as a mixture of Ni metal (ASTM 4-0850), Ni_3S_2 (ASTM 8-126) and carbon (ASTM 26-1081).

$Cu(p\text{-TS})(OH)_3$

In static air (Fig. 3(a))

Copper hydroxy-*p*-toluenesulphonate is anhydrous, and is stable up

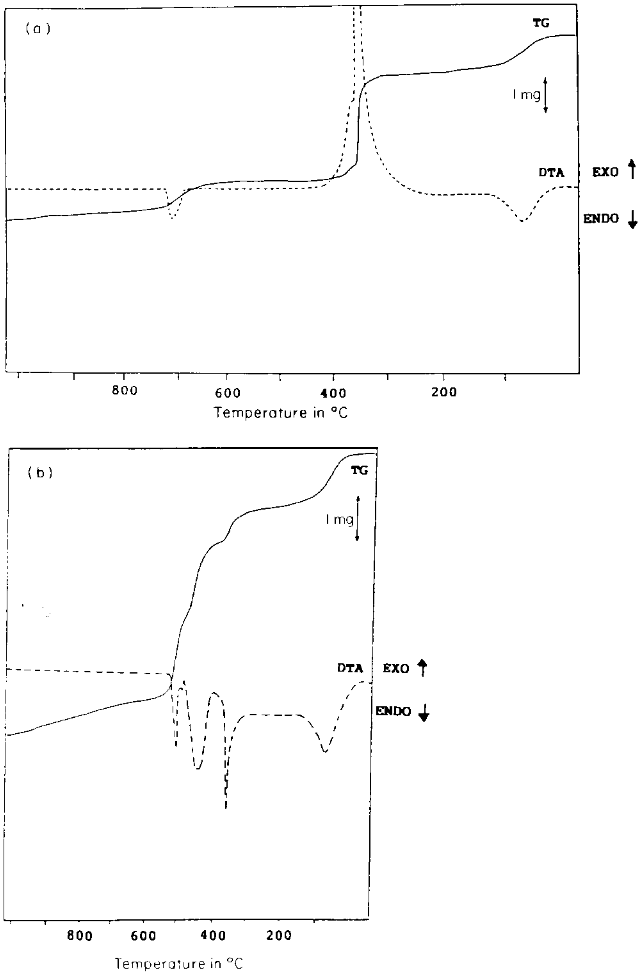

Fig. 2. TG and DTA curves for $Ni_5(p\text{-}TS)_2(OH)_8 \cdot 2H_2O$: (a) in static air; (b) in flowing N_2.

240°C when the dehydroxylation and the organic group combustion begin. The DTA curve shows several simultaneous exothermic effects, ending at 480°C, leading to a mixture of $CuSO_4$ (ASTM 15-775) and CuO (ASTM 5-0661).

Between 600 and 750°C, $CuSO_4$ decomposes, and the final residue obtained was identified as CuO (ASTM 5-0661).

In flowing nitrogen (Fig. 3(b))

The process is very close to that observed in air atmosphere. The compound begin to decompose at about 300°C, and the TG curve shows a continuous weight loss, finishing at 400°C. In the DTA curve, there are three endothermic peaks at ≈280–300, 345, and 900°C, the final degradation product being Cu metal (ASTM 4-0836) with traces of carbon black.

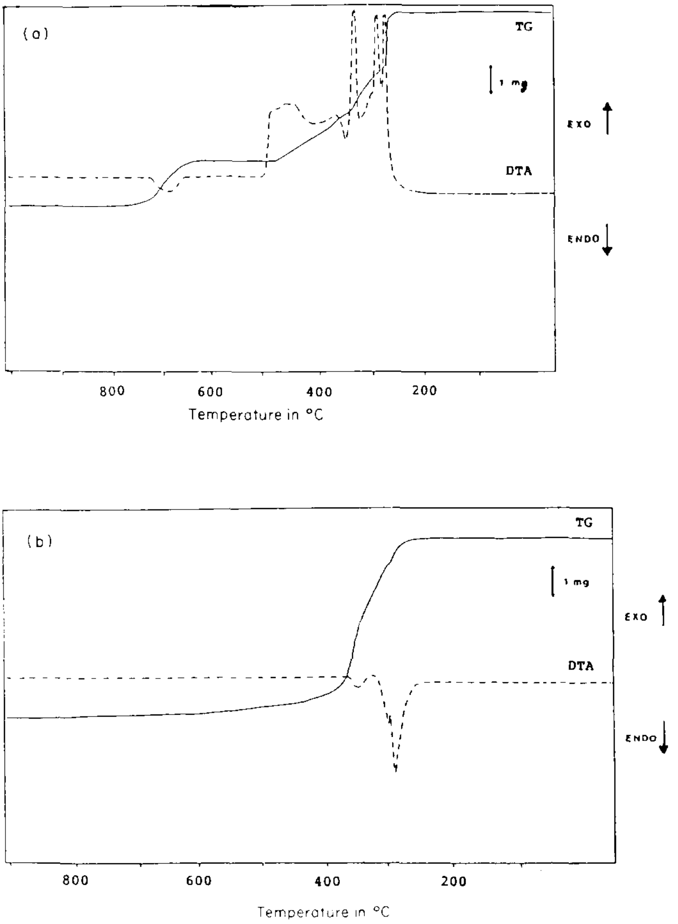

Fig. 3. TG and DTA curves for $Cu_2(p\text{-}TS)(OH)_3$: (a) in static air; (b) in flowing N_2.

$Zn_5(p\text{-}TS)_2(OH)_8 \cdot 4H_2O$

In static air (Fig. 4(a))

The thermogram shows four steps. The dehydration, between room temperature and 140°C, corresponds to a loss of 4 moles of water leading to the formation of the anhydrous hydroxy salt

$$Zn_5(p\text{-}TS)_2(OH)_8 \cdot 4H_2O \rightarrow Zn_5(p\text{-}TS)_2(OH)_8 + 4H_2O$$

(Weight loss: calculated, 8.21%; experimental, 7.8%.)

The dehydroxylation between 140 and 170°C, represents the decomposition of the anhydrous hydroxy salt

$$Zn_5(p\text{-}TS)_2(OH)_8 \rightarrow Zn(p\text{-}TS)_2 + 4ZnO + 4H_2O$$

The solid residue is a mixture of ZnO (ASTM 36-1451) and anhydrous $Zn(p\text{-}TS)_2$. Parallel experiments in an oven have confirmed these results.

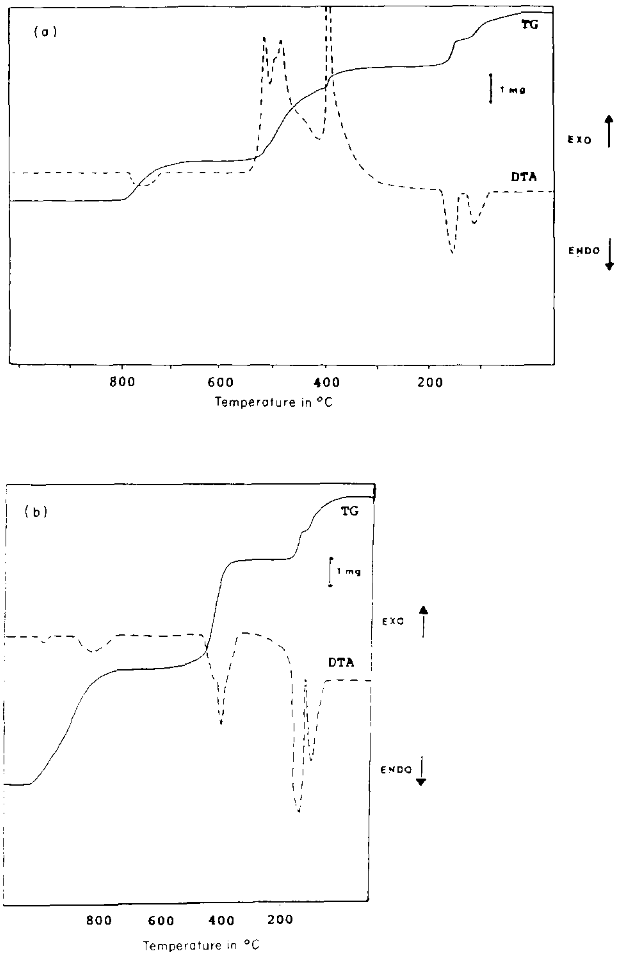

Fig. 4. TG and DTA curves for $Zn_5(p\text{-}TS)_2(OH)_8 \cdot 4H_2O$: (a) in static air; (b) in flowing N_2.

The combustion of the organic group takes place between 330 and 525°C. The DTA curve shows a strong exothermic process with peaks at 393, 482 and 512°C, leading to a mixture of $ZnSO_4$ (ASTM 8-491) and ZnO (ASTM 36-1451).

In TG, the calculated weight loss was 43.2%, and the experimental loss was 44.5%.

At 700°C, $ZnSO_4$ decomposes, and the final residue is ZnO alone (ASTM 36-1451).

In flowing nitrogen (Fig. 4(b))

The thermal degradation of zinc hydroxy-*p*-toluenesulphonate in N_2 occurs in the same way as in air.

In the DTA curve, two successive steps can be seen between room temperature and 145°C, the first corresponding to the elimination of the four water molecules, and the second, between 140 and 200°C, to the dehydroxylation which, however, proceeds through some intermediate plateaus none of which are distinct.

The residue at 250°C is the anhydrous salt which is stable to 540°C, when a decomposition takes place which, according to the XRD data, leads to a mixture of ZnS (ASTM 36-1450) and ZnO (ASTM 36-1451). At 900°C, the final products are ZnS and ZnO with traces of carbon black.

$Cd_2(\text{p-}TS)(OH)_3 \cdot 2H_2O$

In static air (Fig. 5(a))

The dehydration starts at around 95°C and is complete by 140°C, in an

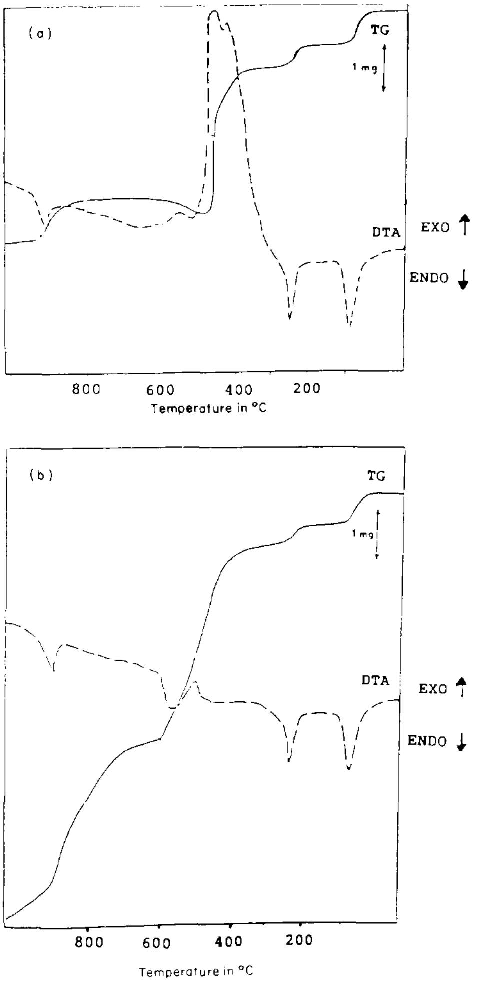

Fig. 5. TG and DTA curves for $Cd_2(p\text{-}TS)(OH)_3 \cdot 2H_2O$: (a) in static air; (b) in flowing N_2.

endothermic process

$Cd_2(p\text{-}TS)(OH)_3 \cdot 2H_2O \rightarrow Cd_2(p\text{-}TS)(OH)_3 + 2H_2O$

The average weight loss is 6.51% while the calculated value is 7.45%.

The anhydrous hydroxy salt is stable up to about 250°C, when another endothermic effect leads to the formation of a cadmium oxy-*p*-toluenesulphonate

$Cd_2(p\text{-}TS)(OH)_3 \rightarrow Cd_2(p\text{-}TS)O_{1.5} + 1.5H_2O$

(Weight loss: calculated, 6.04%; experimental, 6.16%.)

The oxy salt is stable to 400°C. Between this temperature and about 550°C, a strong exothermic effect is seen, corresponding to the thermal degradation of the organic radical with the formation of a cadmium oxysulphate $2CdO \cdot CdSO_4$, (ASTM 32-140), identified by X-ray diffraction.

Finally, at 930°C, an endothermic peak indicates the formation of CdO (ASTM 5-0640) as a solid product

$2CdO \cdot CdSO_4 \rightarrow 3CdO + SO_3$

In flowing nitrogen (Fig. 5(b))

As can be seen, the two first steps, dehydration and dehydroxylation, are very close to those seen in air atmosphere.

The third step between 520 and 640°C, seen as a group of several endothermic effects in the DTA curve, corresponds to the anion decomposition. The TG curve shows a continuous weight loss and the residue is a mixture of CdS (ASTM 6-0314) and CdO (5-0640), according to the XRD data.

The fourth step at about 850°C, with an endothermic peak in the DTA, leads to an amorphous residue at 900°C.

*Pb(*p*-TS)(OH)*

In static air (Fig. 6(a))

Pb(*p*-TS)(OH) is anhydrous, and is stable up to 155°C. The dehydroxylation takes place between 155 and 190°C, yielding the oxysulphonate $Pb_2(p\text{-}TS)_2O$; this has not been described in the literature

$Pb(p\text{-}TS)OH \rightarrow 0.5Pb_2(p\text{-}TS)_2O + 0.5H_2O$

(Weight loss: experimental, 2.6%; calculated, 2.3%.)

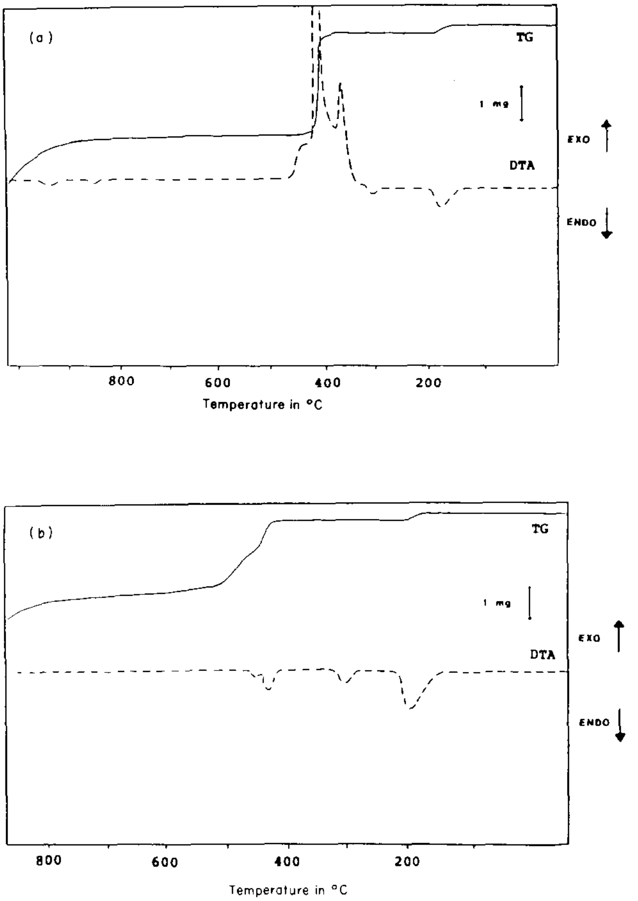

Fig. 6. TG and DTA curves for Pb(*p*-TS)(OH): (a) in static; (b) in flowing N_2.

The DTA curve shows an exothermic peak at 192°C. At 304°C, there is another peak corresponding to a reversible polymorphic transition that takes place between room temperature and the decomposition temperature.

The oxysulphonate decomposes at 375°C, with a strong exothermic effect on the DTA curve between 375 and 425°C, corresponding to the formation of the oxysulphate Pb_2SO_4O (ASTM 6-0276). (Weight loss: experimental, 32.15%; calculated, 33.4%.)

The oxysulphate Pb_2SO_4O decomposes at about 900°C and the final residue is PbO (ASTM 5-0570).

In flowing nitrogen (Fig. 6(b))

The dehydroxylation process occurs in the same way as in air, but at the higher temperature of 170–200°C.

$$\mathrm{Pb}(p\text{-TS})\mathrm{OH} \rightarrow 0.5\mathrm{Pb}_2(p\text{-TS})_2\mathrm{O} + 0.5\mathrm{H}_2\mathrm{O}$$

(Weight loss: experimental, 2.1%; calculated, 2.3%.)

The endothermic DTA peak is at 192°C. As in air, there is a peak at 304°C corresponding to a reversible polymorphic transition between room and decomposition temperatures.

The oxysulphonate decomposes at 410°C in two successive steps (endothermic DTA effects DTA at 430 and 453°C, respectively), leading to the formation at 515°C of PbS (ASTM 5-0592).

Pb_2(p-TS)$(OH)_3$

In static air (Fig. 7(a))

This hydroxy salt exhibits a behaviour similar to that of Pb(*p*-TS) (OH); it is also anhydrous. The first step is the dehydroxylation between room temperature and 210°C. The final residue of this process is the oxysulphon-

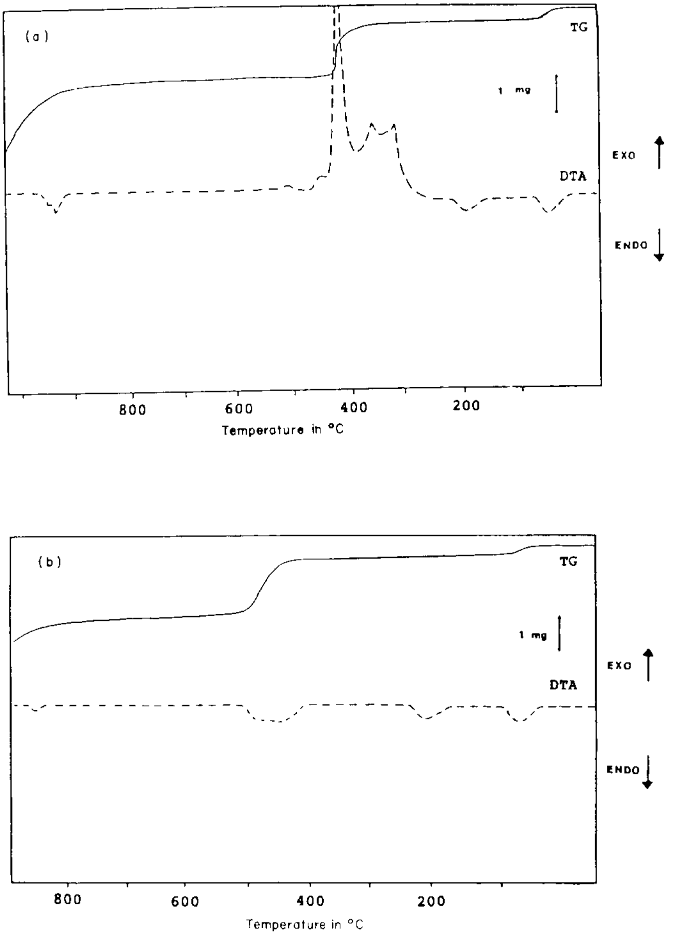

Fig. 7. TG and DTA curves for Pb_2(*p*-TS)$(OH)_3$: (a) in static air; (b) in flowing N_2.

ate $Pb_4(p\text{-}TS)_2O_3$

$Pb_2(p\text{-}TS)(OH)_3 \rightarrow 0.5Pb_4(p\text{-}TS)_2O_3 + 1.5H_2O$

(Weight loss: experimental, 3.93%; calculated, 4·5%.)

The decomposition of $Pb_4(p\text{-}TS)_2O_3$ starts at 400°C, and from 455°C the residue is a mixture of PbO (ASTM 5-0570) and the oxysulphate (ASTM 6-0283) in a ratio of 3:1. The oxysulphate decomposes at about 800°C and the PbO begins to sublime.

In flowing nitrogen (Fig. 7(b))

The dehydroxylation starts at about 80°C and ends at 215°C. The final residue of this process is, as in air, the oxysulphonate $Pb_4(p\text{-}TS)_2O_3$.

From 420°C, the oxysulphonate transforms to a mixture of PbS (ASTM 5-0592) and PbO (ASTM 5-0570)

$Pb_4(p\text{-}TS)_2O_3 \rightarrow 2PbS + 2PbO$

ACKNOWLEDGEMENT

The authors thank Repsol Quimica S.A. for financial support.

REFERENCES

1 F. Charbonnier, Thermochim. Acta, 7 (1973) 217.
2 T. Meisel, Cs. Melykuti and Z. Halmos, J. Therm. Anal., 9 (1976) 261–270.
3 A. Guerrero Laverat, A. Ramírez García, A. Jerónimo, A. Santos, F. Florencio, S. Martinez-Carrera and S. García-Blanco, Inorg. Chim. Acta, 128 (1987) 113–117.
4 A. Jerónimo Varela, A. Guerrero Laverat, M. A. Santos, A. Ramírez García, F. Florencio, S. Martinez-Carrera and S. García-Blanco, An. Quim., 84B (1988) 194–197.
5 M.A. Martinez-Zaporta, L.A. Guerrero, A. Ruiz Amil, S. Martinez-Carrera and S. García-Blanco, An. Quim., 84B (1988) 201–206.
6 A. Guerrero Laverat, A. Ramírez García, A. Santos, M. Bombin, M.A. Martinez-Zaporta, F. Florencio, S. Martinez-Carrera and S. García-Blanco, An. Quim., 86 (1990) 886–891.
7 G.A. Ramírez, A.J. Aycart, L.A. Guerrero and M.A. Jérez, Journées de Calorimétrie d'Analyse Thermique, Ferrara, Italy, 1986.
8 A. Ramírez García, M.L. Gómez-Agüero, A. Guerrero Laverat and M.A. Jeréz, Thermochim. Acta, 124 (1988) 9–16.
9 M. Bombín, L.A. Guerrero, M.A. Martinez-Zaporta, G.A. Ramírez and A. Jeréz, Thermochim. Acta, 146 (1989) 341–352.
10 L.A. Guerrero, G.A. Ramírez, M. Ragel and A. Jeréz, Thermochim. Acta, 213 (1993) 199–210.
11 A. Guerrero Laverat, A. Fálder Rivero and E. Gutierrez Ríos, An. Quim., 75 (1979) 205.
12 A. Guerrero Laverat, A. Fálder Rivero and E. Gutierrez Ríos, An. Quim., 75 (1972) 209.
13 A. Guerrero Laverat, A. Fálder Rivero and E. Gutierrez Ríos, An. Quim., 75 (1979) 213.